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On the problem of the stabilization of α-metallocenylcarbocation. Synthesis, properties and crystal structure of $[C_5Me_5\overline{OsC_5Me_4C}H_2{}^+]BPh_4{}^- \cdot CH_2Cl_2$

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Abstract

The compound, $[C_5Me_5\overline{OsC_5Me_4C}H_2{}^+]BPh_4 \cdot CH_2Cl_2$, has been prepared by the reaction of $C_5Me_5OsC_5Me_4CH_2OH$ with $NaBPh_4$ in acetic acid. The Os...C distance of 2.244 Å and the inclination angle (β) of 41.8° of the exocyclic C(1)–C(2) bond to the Cp-plane found by single-crystal X-ray diffraction study (the crystal was grown from a Et_2O/CH_2Cl_2 (mixture) suggest that there is a covalent Os–C bond. Thus the $C_\alpha(2)$ atom loses its carbenium character, the positive charge being localized mainly around the metal atom which in this case plays a role of the specific onium center.

It has been shown that in nonamethylmetallocenylcarbonium ions the role of direct interaction with the metal atom in the stabilization of α-carbenium cationic center increases in the order Fe < Ru < Os.

The phenomenon of carbenium center stabilization by transition metal complex fragments has received considerable attention during the past 30 years (for reviews see ref. 1 and 2). However, all the questions in this field, especially those concerning the primary ions, could not be completely elucidated because direct structural results, in particular from X-ray diffraction studies, are limited to the stable ions, viz. the secondary differrocenylcarbenium [3] and tertiary diphenylferrocenylcarbenium [4] ions. However, for the unstable primary cations only indirect spectral data are available, and their interpretation is often contradictory. It was deemed worthwhile to approach the problem of stabilization of organometallic carbenium ions by taking as an example the more stable primary carbenium ions derived from nonamethyl-substituted metallocenes. It was important to study not only the ferrocene complexes but also the osmocene and ruthenocene derivatives, because the problem of α-carbenium centers stabilization could be based on a larger number of

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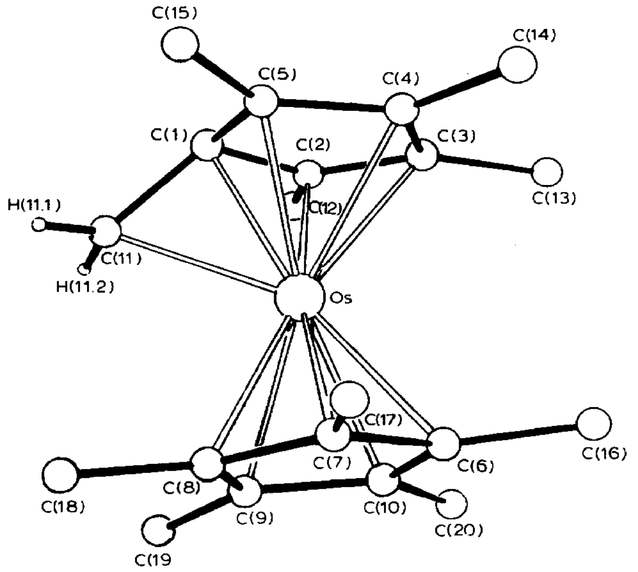

Fig. 1. The structure of cation I.

analogous compounds, with different substituents at the carbenium center, but belonging to the same group of metal atoms. For this purpose nonamethylmetallocenyl carbinols of the iron subgroup were synthesized and their conversion into the corresponding carbenium ion was studied. As a result, a series of cations was prepared, of which the ruthenium and osmium containing ions proved to be the most stable [5–10].

We have carried out a X-ray diffraction study on the stable nonamethylruthenocenylcarbenium hexafluorophosphate [8,9] which revealed a rather strong ruthenium-carbenium center interaction. However the Ru...C^+ distance significantly exceeds that of the Ru–C covalent bond [8,9].

In the present paper we report the synthesis * and some properties of the osmium analogue of the above-mentioned ruthenium cation, viz. nonamethylosmocenylcarbenium ion, and the results of the X-ray study of its tetraphenylborate salt.

The salt is readily formed by mixing the solutions of nonamethylosmocenyl carbinol and $NaBPh_4$ in acetic acid. It was purified by reprecipitation from the CH_2Cl_2 solution with ether, single crystals of the solvate $[C_5Me_5OsC_5Me_4{}^+CH_2]$-$BPh_4{}^- \cdot CH_2Cl_2$ (I) were obtained by slow evaporation of the solvent from the Et_2O/CH_2Cl_2 solution between -5 and $-8\,°C$.

The structure of the cation in salt I is shown in Fig. 1 and the relative arrangement of the tetraphenylborate anion and the methylene chloride solvate molecule is shown in Fig. 2. Bond lengths and angles are listed in Tables 1 and 2.

The geometry of the cation I reveals the strongest interaction of the metal atom with the carbenium center of all metallocenylcarbenium derivatives structurally studied hitherto. Indeed the Os–C(11) distance of 2.244(5) Å in I is even shorter than some Os–C distances to the cyclopentadienyl ring (Os–C(3) 2.264(4), Os–C(4)

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* A preliminary report on the synthesis has been published [10].

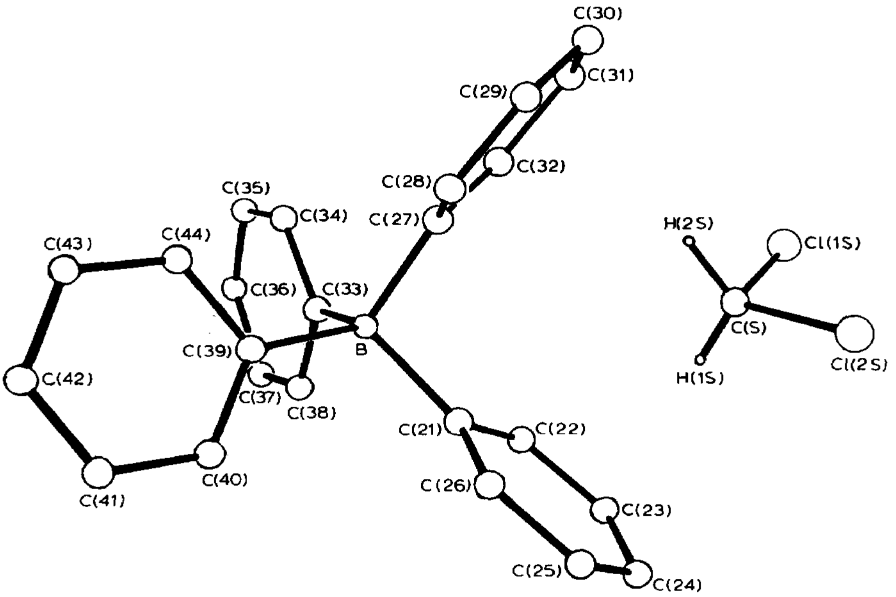


Fig. 2. The relative disposition of the BPh_4^--anion and the solvating CH_2Cl_2 molecule in structure I.

2.269(4) Å). This situation differs markedly from that found in the nonamethylruthenocenylcarbenium ion where, in spite of the significant inclination of the C(Cp)–$\overset{+}{C}$ bond towards the plane of the Cp ligand (β 14°), the Ru... $\overset{+}{C}_\alpha$ distance of 2.603 Å is much greater than that of the covalent Ru–C bond [8,9]. The Os–$\overset{+}{C}_\alpha$(11)

Table 1

Bond lengths *d* (Å) [a] in $[C_5Me_5OsC_5Me_4\overset{+}{C}H_2]BPh_4^-$ (I)

Bond	*d*	Bond	*d*	Bond	*d*
Os–C(1)	2.069(4)	C(6)–C(10)	1.435(7)	C(27)–C(32)	1.394(5)
Os–C(2)	2.187(5)	C(6)–C(16)	1.491(7)	C(28)–C(29)	1.386(6)
Os–C(3)	2.264(4)	C(7)–C(8)	1.414(7)	C(29)–C(30)	1.378(6)
Os–C(4)	2.269(4)	C(7)–C(17)	1.499(7)	C(30)–C(31)	1.377(7)
Os–C(5)	2.181(4)	C(8)–C(9)	1.451(6)	C(31)–C(32)	1.392(6)
Os–C(6)	2.222(4)	C(8)–C(18)	1.497(6)	C(33)–C(34)	1.402(6)
Os–C(7)	2.225(4)	C(9)–C(10)	1.432(6)	C(33)–C(38)	1.407(7)
Os–C(8)	2.193(4)	C(9)–C(19)	1.504(7)	C(34)–C(35)	1.389(7)
Os–C(9)	2.194(4)	C(10)–C(20)	1.490(7)	C(35)–C(36)	1.384(8)
Os–C(10)	2.221(4)	C(11)–H(11.1)	0.99(5)	C(36)–C(37)	1.380(8)
Os–C(11)	2.244(5)	C(11)–H(11.2)	0.91(5)	C(37)–C(38)	1.371(7)
C(1)–C(2)	1.470(6)	B–C(21)	1.651(6)	C(39)–C(40)	1.402(6)
C(1)–C(5)	1.461(7)	B–C(27)	1.647(6)	C(39)–C(44)	1.396(6)
C(1)–C(11)	1.426(7)	B–C(33)	1.637(7)	C(40)–C(41)	1.383(6)
C(2)–C(3)	1.403(7)	B–C(39)	1.646(6)	C(41)–C(42)	1.369(6)
C(2)–C(12)	1.492(8)	C(21)–C(22)	1.399(6)	C(42)–C(43)	1.381(6)
C(3)–C(4)	1.439(6)	C(21)–C(26)	1.388(6)	C(43)–C(44)	1.392(6)
C(3)–C(13)	1.502(6)	C(22)–C(23)	1.388(6)	C(S)–Cl(1S)	1.754(5)
C(4)–C(5)	1.413(6)	C(23)–C(24)	1.380(7)	C(S)–Cl(2S)	1.747(6)
C(4)–C(14)	1.509(7)	C(24)–C(25)	1.386(7)	C(S)–H(1S)	0.85(5)
C(5)–C(15)	1.486(7)	C(25)–C(26)	1.395(6)	C(S)–H(2S)	1.01(5)
C(6)–C(7)	1.449(6)	C(27)–C(28)	1.397(6)		

[a] Bonds involving all non-hydrogen atoms as well as the H(11.1), H(11.2), H(1S) and H(2S) are listed.

Table 2

Bond angles (degrees) [a] in $[C_5Me_5OsC_5Me_4{}^+CH_2]BPh_4{}^-$ (I)

Angle		Angle		Angle	
C(2)C(1)C(5)	109.3(4)	C(10)C(9)C(19)	125.9(4)	C(29)C(30)C(31)	119.5(4)
C(2)C(1)C(11)	116.0(4)	C(6)C(10)C(9)	108.0(4)	C(30)C(31)C(32)	119.7(4)
C(5)C(1)C(11)	116.1(4)	C(6)C(10)C(20)	125.8(4)	C(27)C(32)C(31)	123.1(4)
C(1)C(2)C(3)	105.8(4)	C(9)C(10)C(20)	126.1(4)	BC(33)C(34)	123.0(4)
C(1)C(2)C(12)	127.0(4)	C(1)C(11)H(11.1)	116(3)	BC(33)C(38)	122.4(4)
C(3)C(2)C(12)	127.1(4)	C(1)C(11)H(11.2)	120(3)	C(34)C(33)C(38)	114.5(4)
C(2)C(3)C(4)	109.6(4)	H(11.1)C(11)H(11.2)	120(4)	C(33)C(34)C(35)	122.9(4)
C(2)C(3)C(13)	125.5(4)	C(21)BC(27)	103.1(3)	C(34)C(35)C(36)	119.8(5)
C(4)C(3)C(13)	124.8(4)	C(21)BC(33)	112.1(3)	C(35)C(36)C(37)	119.1(5)
C(3)C(4)C(5)	109.9(4)	C(21)BC(39)	113.6(3)	C(36)C(37)C(38)	120.3(5)
C(3)C(4)C(14)	125.3(4)	C(27)BC(33)	112.7(3)	C(33)C(38)C(37)	123.4(4)
C(5)C(4)C(14)	124.8(4)	C(27)BC(39)	110.4(3)	BC(39)C(40)	125.7(4)
C(1)C(5)C(4)	105.4(4)	C(33)BC(39)	105.2(3)	BC(39)C(44)	119.1(4)
C(1)C(5)C(15)	125.8(4)	BC(21)C(22)	122.5(4)	C(40)C(39)C(44)	115.1(4)
C(4)C(5)C(15)	128.7(4)	BC(21)C(26)	122.2(4)	C(39)C(40)C(41)	122.1(4)
C(7)C(6)C(10)	107.8(4)	C(22)C(21)C(26)	114.9(4)	C(40)C(41)C(42)	121.3(4)
C(7)C(6)C(16)	125.6(4)	C(21)C(22)C(23)	123.0(4)	C(41)C(42)C(43)	118.7(4)
C(10)C(6)C(16)	126.6(4)	C(22)C(23)C(24)	120.0(4)	C(42)C(43)C(44)	119.9(4)
C(6)C(7)C(8)	108.2(4)	C(23)C(24)C(25)	119.2(4)	C(39)C(44)C(43)	122.9(4)
C(6)C(7)C(17)	125.6(4)	C(24)C(25)C(26)	119.3(4)	Cl(1S)C(S)Cl(2S)	112.0(3)
C(8)C(7)C(17)	126.3(4)	C(21)C(26)C(25)	123.5(4)	Cl(1S)C(S)H(1S)	112(3)
C(7)C(8)C(9)	108.2(4)	BC(27)C(28)	121.6(4)	Cl(1S)C(S)H(2S)	107(3)
C(7)C(8)C(18)	124.7(4)	BC(27)C(32)	123.2(4)	Cl(2S)C(S)H(1S)	107(3)
C(9)C(8)C(18)	126.8(4)	C(28)C(27)C(32)	114.8(4)	Cl(2S)C(S)H(2S)	103(3)
C(8)C(9)C(10)	107.7(4)	C(27)C(28)C(29)	123.2(4)	H(1S)C(S)H(2S)	116(4)
C(8)C(9)C(19)	126.1(4)	C(28)C(29)C(30).	119.7(4)		

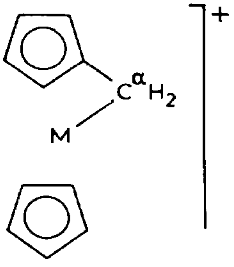
[a] Bond angles involving all non-hydrogen atoms as well as the H(11.1), H(11.2), H(1S), H(2S) atoms are listed.

distance in the cation I is close to the Os–C σ-bond length of 2.22 Å [13], thus the $C_\alpha(11)$ atom is deprived of its carbenium character and the positive charge is essentially localized about the metal atom which plays the role of specific onium center. Such close approach of the Os and C(11) atoms is due: (i) to the shift of the metal atom relative to the center of the cyclopentadienyl ring towards the C(1) and C(11) atoms (the distance from the Os atom projection onto the C(1)–C(5) ring plane to the center of the ring is equal to 0.20 Å) and (ii) to the inclination of the C(1)–C(11) bond to the plane of the C(1)–C(5) ring (the displacement of the C(11) atom from this plane being 0.961(5) Å, all other exocyclic methyl carbon atoms are displaced from the planes of the Cp rings in the direction away from the Os atom by 0.02–0.12 Å). In I the angle between the exocyclic C(1)–C(11) bond and the plane of the C(1)–C(5) ring (β 41.8°) is larger than the corresponding angles in all the carbenium ionic systems previously studied [3,4,8,9]: the closest value β 39° was found in a metal complex of the same third long period, viz. $(\eta^6\text{-}MeC_6H_5)W(C_5H_4CPh_2)$ [11].

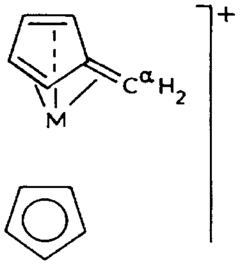
The shift of the metal atom in the direction of the $C(1)–C_\alpha(11)$ bond and the displacement of the C(11) atom from the Cp ring plane towards the metal atom results in some redistribution of bond lengths in the organic ligand. Thus the exocyclic C(1)–C(11) bond length of 1.426(7) Å differs only slightly from the lengths of double bonds coordinated by metal atoms in π-olefinic complexes (e.g. 1.40 Å in $Fe(CO)_4(\eta^2\text{-}CH_2{=}CHCN)$ [12]); the C(1)–C(11) bond is noticeably shorter than the nine other C_{Cp}–C_{Me} distances in I (1.486–1.509 Å). The differences in bond lengths of the 5-membered C(1)–C(5) cycle are also distinct but not as significant, viz. the C(1)–C(2) 1.470(6), C(1)–C(5) 1.461(7) and C(3)–C(4) 1.439(6) Å bonds are somewhat longer than the C(2)–C(3) 1.403 (7) and C(4)–C(5) 1.413(6) Å bonds. Such differences in bond lengths are quite characteristic of the systems discussed and have been observed in all the fulvene complexes of Cr, Mo and W studied previously [11,13–15].

Just as in case of the Fe,-Cr, Mo and W complexes [11,13–15] no distortion of the planarity of the 5-membered cycle bonded to the carbenium center is observed in I: the displacement of the C(1) atom from the C(2)C(3)C(4)C(5) plane is not greater than 0.024(4) Å, the dihedral angle between this and the C(2)C(1)C(5) plane being 1.6(5)°. In cation I the planes of the C(1)–C(5) and C(6)–C(10) cycles are not quite parallel, and this is evidently caused by the interaction of $C_\alpha(11)$ with the Os atom. Nevertheless the dihedral angle formed by these planes is small (6.9(2)°), while in ferrocenylcarbenium cation [4], in which the M... C_α distance is longer by 0.5 Å than in I, the inclination angle is much larger (9.3°).

As a result of extensive discussions on the mechanism of stabilisation of the carbenium ionic center in α-metallocenylcarbenium systems (for reviews see refs. 1 and 2) and two forms of bonding were proposed:

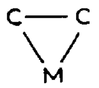


(A)

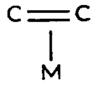


(B)

When the above-mentioned redistribution of bond lengths in the organic ligand is taken into account some authors prefer structure **B** with the fulvene-type ligand. However, considerable displacement of the C_α atom from the cyclopentadienyl ring plane towards the metal atom and the observed bond lengths and angles do not exclude the alternative version in which the metal atom is bonded to the organic ligand as in structure **A**. This type of coordination has been designated as σ-η^5 [11]. The question which of the two schemes is to be preferred seems to be academic and is similar to that of which of the two schemes of π-bonding of olefins is the better:

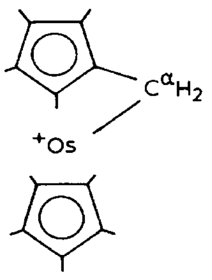


(C)

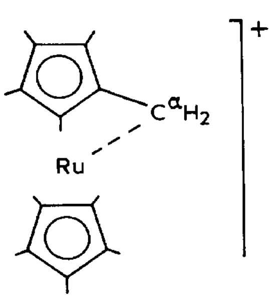


(D)

We chose formula I of type A, because it seems to be the more illustrative, but we are aware of the limitations of both suggestions for the interaction between the carbenium center and the metal atom in α-metallocenylcarbenium ions.



(I)



(II)

However we adopted formula II for the ruthenium complex because the metal–$\overset{+}{C}_\alpha$ interaction is much weaker and the Ru... $\overset{+}{C}_\alpha$ distance is considerably longer than the corresponding covalent bond.

The X-ray data for the diferrocenyl- [3] and diphenylferrocenylcarbenium ions [4], the NMR data and the likelihood that there is singlet $\rightleftarrows$ triplet transition in these ions described previously [5–7] confirm that the M... C_α^+ interaction in the ferrocene series is even weaker. Thus it may be assumed that in similar ruthenium- and iron-containing ions there is no covalent M–C_α^+ bond but a strong secondary M... C_α^+ interaction.

In the series of the cations, containing iron, ruthenium or osmium atoms, the interaction of the carbenium center with the metal atom changes from weak to very strong on going down group 8. This leads to the important conclusion that the contribution to α-carbenium ionic center stabilization because of direct interaction with the metal atom also increases down the group 8. This phenomenon can be explained in terms of the increase in the size and basicity [18–20] i.e. the nucleophility of the metal atom * down the sub-group.

The X-ray study data for I revealed some unusual features in its structure. Firstly the staggered conformation of the cyclopentadienyl rings presumably also caused by the Os–C_α(11) interaction is noteworthy. Indeed theoretical considerations [21] later corroborated by the X-ray structural study [22] have shown that, in contrast to its iron analogue, the eclipsed conformation of the Cp rings is preferred in decamethylosmocene. The staggered conformation of I (torsion angle C(1)Cp(1)Cp(2)C(6) ** is $-177.6(6)°$) is probably due to steric factors, which in the eclipsed conformation would not have allowed the significant displacement of the C(11) atom towards the metal atom mentioned above.

Another interesting feature of the crystal structure of I is the specific relative arrangement of the tetraphenylborate anion and the solvating CH_2Cl_2 molecule. As can be seen from Fig. 2, the C atom of the CH_2Cl_2 lies in the plane bisecting the dihedral angle of the planes of the two Ph substituents of the BPh_4^- anion. The hydrogen atoms H(1S) and H(2S) of the CH_2Cl_2 molecule are located over the corresponding Ph cycles at approximately equal distances from each of their carbon atoms. Although the H(1S)...C(21–26) (2.79–2.98 Å) and H(2S)...C(27–32) (2.65–2.97 Å) distances are in fact close to the sum of the H and C Van der Waals radii ($1.20 + 1.70 = 2.90$ Å [23]) the conformation of the BPh_4^- anion and the way

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* Covalent radii are equal to 1.34 Å for Fe, 1.48 Å for Ru, 1.60 Å for Os [18].

** Cp(1) and Cp(2) are the centroids of the C(1)–C(5) and C(6)–C(10) rings, respectively.

in which the anion associates with the CH_2Cl_2 molecule indicates that there is an interaction between them. A similar $BPh_4^- \ldots H_2O$ interaction has been found in the structure of $[n\text{-}Bu_3{}^+NH]BPh_4^- \cdot H_2O$ [24]. The authors have proved the existence of such interaction, which they suggested to be an $OH \ldots \pi$ hydrogen bond, not only from the X-ray data but also on the basis of the IR data. Given the appreciable C–H acidity of the CH groups in the CH_2Cl_2 molecule due to the polarity of C–Cl bonds, one may expect these groups to act as donors in H bonds. From this point of view the interaction found in complex I may be considered as H bonds of the $CH \ldots \pi$ type analogous to those of the type $OH \ldots \pi$; to our knowledge there have been no previous X-ray data to confirm the existence of the $CH \ldots \pi$ bonds.

In order to investigate the chemical properties of I its reactions with such strong nucleophilic agents such as trimethylamine * and dimethylphenylphosphine were studied. The reactions proceed readily, and as in the case of other onium compounds the corresponding onium products are formed. The amine and phosphine alkylation by I indicates the lower nucleophility of the Os atom in the decamethylosmocene in comparison with the tertiary amine and phosphine. The composition and the structure of the dimethylphenyl-α-nonamethylosmocenylphosphonium salt have been confirmed by elemental analysis and by ^1H, ^{31}P and ^{13}C NMR spectroscopy.

Experimental

Preparation of $[C_5Me_5\overline{OsC_5Me_4C}H_2]^+BPh_4^-$ ** *(I).* A solution of 0.17 g (0.5 mmol) of $NaBPh_4$ in 20 ml of absolute AcOH was added with stirring to a solution of 0.24 g (0.5 mmol) of $C_5Me_5OsC_5Me_4CH_2OH$ [10] in 40 ml of absolute AcOH. The precipitate formed was washed twice with 5 ml portions of AcOH and three times with 10 ml portions of absolute Et_2O, dissolved in CH_2Cl_2 and precipitated by 100 ml of absolute Et_2O. The precipitate was isolated by filtration, washed with ether and dried in vacuum. The yield was 0.29 g (74.5%). ^1H NMR ($CDCl_3$): 6.8–7.3 (m,Ph,20H), 4.398 (s,CH_2^+,2H), 1.909 (s,C_5Me_5,15H), 1.847, 1.599 (s,s,C_5Me_4,6H,6H). ^{13}C NMR (CH_2Cl_2) ***: 99.85, 90.78, 84.43 (C_5Me_4), 92.69 (C_5Me_5), 55.40 (CH_2^+), 9.23 (C_5Me_5), 8.92, 7.84 (C_5Me_4).

Reaction of I with PMe_2Ph. To a solution of 0.22 g of $[C_5Me_5\overline{OsC_5Me_4C}H_2]^+$ BPh_4^- (0.28 mmol) in 30 ml of CH_2Cl_2 was added 1 ml of PMe_2Ph. The mixture was stirred for 3 h and then the volume reduced to 7–8 ml; 50 ml of absolute Et_2O was added to the residue. The precipitate was filtered off, dissolved in the minimum amount (5 ml) of CH_2Cl_2 and precipitated by absolute ether. The yield of $[C_5Me_5OsC_5Me_4CH_2{}^+PPhMe_2]BPh_4^-$ was 0.25 g (96%). ^1H NMR (CD_2Cl_2): 6.8–7.8(m, $^+$P–Ph, B–Ph, 5H, 20H), 2.64(d, *J* 10.1 Hz, CH_2–P^+), 1.64 (s, C_5Me_5), 1.33, 1.67 (s, s, C_5Me_4), 1.24 (d, *J* 13.2 Hz, P^+–Me); ^{31}P NMR 22.84; ^{13}C NMR 165.8, 163.8, 162.8, 136.1, 135.1, 134.5, 130.4, 126.0, 122.0, 120.0, 118.3 ($C_{aromatic}$),

(*Continued on p. 242*)

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* The corresponding ammonium salt is now being investigated.

** The yields and the mmol values are calculated for the $[C_5Me_5\overline{OsC_5Me_4C}H_2]^+$ BPh_4^-, the solvating CH_2Cl_2 molecule was not taken into account.

*** The ^{13}C NMR spectrum for $[C_5Me_5\overline{OsC_5Me_4C}H_2]^+$ PF_6^- is reported in ref. 10.

Table 3

Atomic coordinates ($\times 10^4$, for Os$\times 10^5$, for H$\times 10^3$) and their equivalent isotropic (isotropic for H atoms) temperature factors for $[C_5Me_5OsC_5Me_4CH_2{}^+]BPh_4{}^-$ (I)

Atom	x	y	z	B_{eq}/B_{iso} (Å^2)	Atom	x	y	z	B_{iso} (Å^2)
Os	2476(1)	32945(1)	27896(1)	1.61(1)	H(11.2)	−201(4)	402(3)	234(3)	2.1(9)
C(1)	−230(4)	3439(4)	1503(3)	2.6(1)	H(12.1)	−99(5)	110(5)	268(4)	5(1)
C(2)	−64(4)	2262(4)	1847(3)	2.6(1)	H(12.2)	−190(5)	217(5)	221(4)	6(1)
C(3)	1208(4)	1851(3)	1881(3)	2.2(1)	H(12.3)	−102(5)	128(4)	152(4)	6(1)
C(4)	1842(4)	2715(3)	1495(3)	2.2(1)	H(13.1)	254(5)	63(4)	239(4)	5(1)
C(5)	980(4)	3707(3)	1273(3)	2.5(1)	H(13.2)	127(6)	36(5)	266(4)	7(2)
C(6)	1147(4)	2927(4)	4005(3)	2.4(1)	H(13.3)	209(7)	13(6)	159(5)	9(2)
C(7)	899(4)	4108(3)	3734(3)	2.1(1)	H(14.1)	334(4)	324(4)	146(3)	3.7(9)
C(8)	−411(4)	4541(3)	3850(3)	2.1(1)	H(14.2)	356(4)	194(4)	179(3)	3.3(9)
C(9)	−1006(4)	3641(3)	4214(3)	2.2(1)	H(14.3)	364(5)	240(4)	70(4)	4(1)
C(10)	−37(4)	2650(4)	4313(3)	2.3(1)	H(15.1)	45(4)	543(4)	101(3)	4(1)
C(11)	−1271(4)	4206(4)	2056(3)	3.1(1)	H(15.2)	166(5)	467(4)	16(4)	5(1)
C(12)	−1033(5)	1624(5)	2086(4)	4.2(2)	H(15.3)	180(4)	494(3)	100(3)	2.8(9)
C(13)	1832(5)	676(4)	2137(3)	3.1(1)	H(16.1)	310(4)	234(3)	352(3)	2.2(9)
C(14)	3233(4)	2575(4)	1338(3)	3.1(1)	H(16.2)	257(5)	212(4)	457(3)	4(1)
C(15)	1228(5)	4783(4)	828(4)	3.7(2)	H(16.3)	248(5)	139(4)	394(4)	4(1)
C(16)	2407(4)	2158(4)	4006(3)	3.1(1)	H(17.1)	159(5)	539(4)	301(3)	4(1)
C(17)	1870(4)	4754(4)	3402(4)	3.4(2)	H(17.2)	205(6)	505(5)	390(4)	7(2)
C(18)	−1057(5)	5746(4)	3712(3)	3.2(1)	H(17.3)	264(5)	429(4)	319(3)	5(1)
C(19)	−2397(4)	3747(4)	4516(3)	3.0(1)	H(18.1)	−105(4)	616(3)	425(3)	2.9(9)
C(20)	−226(5)	1539(4)	4713(3)	3.5(2)	H(18.2)	−57(5)	611(5)	315(4)	6(1)

B	5315(4)	2886(4)	7875(3)	1.9(1)	H(18.3)	−188(5)	583(4)	364(4)	5(1)
C(21)	5442(4)	2570(3)	6787(3)	1.9(1)	H(19.1)	−282(4)	442(3)	412(3)	2.2(8)
C(22)	6290(4)	1610(3)	6390(3)	2.3(1)	H(19.2)	−259(5)	314(4)	432(4)	5(1)
C(23)	6311(4)	1272(3)	5521(3)	2.7(1)	H(19.3)	−269(5)	387(4)	522(4)	5(1)
C(24)	5476(5)	1896(4)	5005(3)	2.9(1)	H(20.1)	−82(5)	142(4)	463(4)	5(1)
C(25)	4618(4)	2857(4)	5366(3)	2.8(1)	H(20.2)	−40(5)	150(4)	538(4)	5(1)
C(26)	4612(4)	3166(3)	6247(3)	2.1(1)	H(20.3)	43(5)	92(4)	440(3)	4(1)
C(27)	4243(4)	2278(3)	8548(3)	1.6(1)	H(22)	692(4)	115(3)	674(3)	2.6(9)
C(28)	2961(4)	2814(3)	8723(3)	2.1(1)	H(23)	694(4)	57(3)	527(3)	3.1(9)
C(29)	2029(4)	2294(4)	9205(3)	2.5(1)	H(24)	550(4)	168(3)	441(3)	2.4(9)
C(30)	2355(4)	1195(4)	9539(3)	2.5(1)	H(25)	406(4)	334(4)	500(3)	4(1)
C(31)	3606(4)	630(3)	9392(3)	2.3(1)	H(26)	402(4)	383(3)	646(3)	2.2(9)
C(32)	4524(4)	1170(3)	8899(3)	2.0(1)	H(28)	272(4)	357(3)	856(3)	2.1(8)
C(33)	6655(4)	2448(3)	8176(3)	2.1(1)	H(29)	115(4)	268(3)	931(3)	2.6(9)
C(34)	6737(4)	2122(3)	9121(3)	2.4(1)	H(30)	180(4)	87(3)	987(3)	1.7(8)
C(35)	7870(5)	1799(4)	9383(4)	3.3(2)	H(31)	383(4)	−13(4)	957(3)	4(1)
C(36)	8979(5)	1809(4)	8698(4)	4.1(2)	H(32)	531(3)	78(3)	877(3)	1.4(8)
C(37)	8937(4)	2143(4)	7763(4)	3.7(2)	H(34)	595(4)	207(4)	961(3)	3.4(9)
C(38)	7811(4)	2456(4)	7517(3)	2.7(1)	H(35)	788(4)	158(3)	1001(3)	3.1(9)
C(39)	4860(4)	4230(3)	8006(3)	1.8(1)	H(36)	968(4)	158(4)	884(3)	4(1)
C(40)	4986(4)	5067(3)	7267(3)	1.9(1)	H(37)	970(5)	224(5)	730(4)	6(1)
C(41)	4630(4)	6179(4)	7443(3)	2.4(1)	H(38)	784(4)	263(4)	690(3)	4(1)
C(42)	4155(4)	6515(3)	8354(3)	2.4(1)	H(40)	528(3)	485(3)	665(2)	0.6(8)
C(43)	4020(4)	5720(3)	9106(3)	2.6(1)	H(41)	471(4)	667(3)	698(3)	2.4(9)
C(44)	4369(4)	4602(3)	8926(3)	2.4(1)	H(42)	400(4)	728(3)	852(3)	2.1(8)
C(S)	3486(5)	691(4)	7033(3)	3.1(1)	H(43)	374(4)	590(3)	971(3)	2.6(9)
Cl(1S)	4219(2)	−701(1)	7307(1)	4.4(5)	H(44)	433(4)	405(3)	947(3)	2.4(9)
Cl(2S)	2249(1)	815(1)	6515(1)	4.9(5)	H(1S)	400(4)	101(4)	664(3)	2.8(9)
H(11.1)	−127(5)	500(4)	192(4)	4(1)	H(2S)	304(4)	105(4)	766(3)	4(1)

80.4, 79.9, 76.2, 68.2 (C_5Me_5, C_5Me_4), 26.2, 25.3 (CH_2–P^+), 11.4, 10.0(C_5Me_4), 10.2(C_5Me_5), 7.3, 6.2 (P^+–Me). Found: C, 67.33; H, 6.49. $C_{52}H_{60}BPOs$ calc.: C, 68.11; H, 6.43%.

Reaction of I with NMe_3. Gaseous NMe_3 (formed by the dropwise addition of aqueous $Me_3N \cdot HCl$ to the aqueous NaOH, and dried over solid NaOH) was bubbled for 3 h through a solution of 0.2 g (0.26 mmol) of $[C_5Me_5\overline{OsC_5Me_4C}H_2]^+$ BPh_4^- in 30 ml of CH_2Cl_2. As the gas bubbled through a white precipitate steadily formed. The solution was evaporated and the residue was dissolved in the dimethylformamide/acetone (1/1) mixture (10 ml) and precipitated by dry Et_2O. ^1H NMR (CD_3CN) 6.8–7.3 (m, Ph, 20H), 5.27 (CH_2Cl_2), 3.21 (N^+Me_3), 2.92 (CH_2–N^+), 2.34 (NMe_3), 1.82, 1.73 (C_5Me_4), 1.70 (C_5Me_5). Found: C, 59.00; H, 7.16; N, 3.47; Cl, 6.99. $C_{52}H_{69}BN_2Os$ * calc.: C, 59.20; H, 7.00; N, 3.12; Cl, 7.13%.

X-Ray diffraction study. Crystals of I are triclinic, at $-120\,°C$ a 11.482(4), b 12.608(4), c 14.603(5) Å, α 81.60(3), β 73.74(3), γ 73.18(3)°, V 1938(1) Å^3, d_{calc} 1.480 g/cm^3 $Z = 2$, space group $P\bar{1}$. The unit cell parameters and the intensities of 5071 independent reflections with $F^2 \geqslant 4\sigma$ were measured with a four-circle automatic Syntex $P2_1$ diffractometer ($-120\,°C$, λ(Mo-K_α), graphite monochromator, $\theta/2\theta$-scan, $\theta \leqslant 25°$).

The structure was solved by the heavy atom method. The Os atom coordinates were found from a Patterson synthesis, all other non-hydrogen atoms including the Cl and C atoms of the solvate CH_2Cl_2 molecule were located in the subsequent electron density syntheses. After structure refinement by the full-matrix least-squares technique the correction for absorption according to DIFABS [26] was applied (μ(Mo-K_α) 36.6 cm^{-1}) and the refinement was continued at first in the isotropic and then in the anisotropic approximation. All H atoms of the cation, anion and the solvating molecule were located directly in the difference Fourier synthesis and included in the final refinement in the isotropic approximation. The final discrepancy factors are R 0.026 and R_w 0.038. All calculations were carried out using the INEXTL program package [27] with an Eclipse S/200 computer. The atomic coordinates and the temperature factors are listed in Table 3.

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* From the elemental analysis and the ^1H NMR data it was suggested that the product of the interaction of I with NMe_3 represents the solvate with NMe_3 and CH_2Cl_2 $[C_5Me_5OsC_5Me_4CH_2NMe_3]BPh_4^- \cdot NMe_3 \cdot CH_2Cl_2$. Unfortunately the low concentration of the compound (low solubility in CH_2Cl_2, CH_3CN, $(CH_3)_2CO$, $HCON(CH_3)_2$ and CH_3NO_2) prevented us from obtaining a ^{13}C NMR spectrum that could have confirmed the structure.

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